MODIFICATION OF NANOFILLER TO IMPROVE THE FINAL PROPERTIES OF POLYLACTIC ACID (PLA) NANOCOMPOSITES

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ABSTRACT

Modifications of nanoclay were prepared from pristine clays and organoclays with Transition Metal Ions (TMIs), Ferum, Copper and Nickel using different solvents. The first part of the experiment focuses on determining the viability of Ethanol as a solvent in the modification process as well as its efficiency in aiding the adsorption of TMIs in comparison to solvents such as Methanol and Dioxane. The composition and structure of the modified nanoclay were characterized using Atomic Absorption Spectroscopy (AAS), Fourier Transform Infrared (FTIR) and Scanning Electron Microscopy (SEM). From the AAS results, it was determined that Ethanol was a viable solvent for the nanoclay modification and proved to be extremely efficient for Copper ions especially. SEM and FTIR results proved that modified nanoclays had smoother surfaces for pristine clays or montmorilonite (MMT) which proved that the modification was successful. The same modifications performed on organoclayswere proven to be unsuccessful. The modified samples were then intercalated in Polylactic Acid (PLA) polymer matrices to form polymer nanocomposites (PNC). The biodegradability and thermal stability of the Polymer nanocomposites were tested and its performance is compared against a polymer nanocomposite intercalated with pure (unmodified) nanoclay. The PNC were formed using solution intercalation method with 1,4-Dichloroethane as a solvent. Both the biodegradability and thermal stability also showed positive improvements. Biodegradibility is hypothesized to have increased due to the characteristics of transition metal ion which are easily oxidized. The ions with higher electronegativity showed the least improvement when intercalated into the polymer matrices. Thermal stability also increased significantly, due to the transition metal ions hindering the pristine clay within the polymer matrices from decomposing easily. Further research will be required to commercialize findings.

Keywords: Modification, Nanoclay, Montmorillonite, Organoclay, Transition Metal Ions (TMIs), Solution Intercalation, Polylactic Acid (PLA) , Polymer Nanocomposites (PNC), Characterize, Scanning Electron Microscopy (SEM), Atomic Absorption Spectrometry (AAS), Fourier Transform Infrared (FTIR), Thermal Stability, Biodegradibility,

ABSTRAK

Ubahsuaian tanah bersaiz nano (nanoclay);- montmorilonite (*pristine clay*) dan organoclays, dengan Ion Logam Peralihan(TMIs) seperti Ferum, Kuprum dan Nikel menggunakan pelarut yang berbeza telah disediakan. Bahagian pertama eksperimen tertumpu kepada pembuktian kemampuan Etanol sebagai pelarut dalam proses pengubahsuaian serta kecekapan dalam membantu penjerapan TMIs berbanding dengan pelarut seperti Metanol dan Dioxana. Komposisi dan struktur nanoclay yang telah diubah suai dicirikan menggunakan Spektroskopi Serapan Atom (AAS), Fourier Transform Infrared (FTIR) dan Mikroskopi Imbasan Elektron (SEM). Dari keputusan AAS, ia telah ditentukan bahawa Etanol merupakan pelarut yang sesuai digunakan bagi pengubahsuaian nanoclay dan terbukti sebagai sangat efisien untuk penjerapan ion Kuprum terutamanya. Keputusan SEM dan FTIR membuktikan bahawa pengubahsuai montmorillonite(pristine clay) menyebabkan permukaan menjadi lebih licin daripada montmorillonite (MMT) yang asli Keputusan ini tidak sama dengan keputusan yang diperolehi untuk organoclay. Sampel yang diubah suai kemudiannya dicampurkan dalam matriks polimer Polylactic Asid (PLA) untuk membentuk polimer dengan komposit bersaiz nano (PNC). Penguraian Biologik (biodegradability) dan kestabilan haba PNC telah diuji dan dibandingkan dengan prestasi PNC yang telah dicampurakan dengan nanoclay asli (tidak diubahsuai). PNC telah dibentuk menggunakan kaedah interkalasi larutan dengan menggunakan 1,4-Dikloroetana sebagai pelarut. Kedua-dua penguraian biologik dan kestabilan haba juga menunjukkan peningkatan yang positif dari segi persembahan. Penguraian biologik mungkin telah dipercepatkan disebabkan ciri-ciri ion logam peralihan yang mudah dioksidakan. Ion yang lebih elektronegatif menyebakan peguraian lebih lambat apabila diinterkalasi ke dalam matriks polimer. Kestabilan termal juga meningkat dengan ketara, ini kerana ion-ion logam peralihan menghalang nanoclay dalam PNC daripada terurai dengan mudah. Penyelidikan lanjut diperlukan untuk mengkomersilkan penemuan.

Kata Kunci: Pengubahsuaian, Tanah Bersaiz Nano (Nanoclay), Ion Logam Peralihan (Tmis), Interkalasi Larutan, Asid Polylactic (PLA) , Polimer Dengan Komposit Bersaiz Nano (PNC), Dicirikan, Microskopi Imbasan Elektron (SEM), Spektrometri Penyerapan Atom (AAS), Fourier Transform Infrared (FTIR), Kestabilan Terma, Penguraian Biologik

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LIST OF SYMBOLS

%	Percentage
°C	Degree celsius
Min	Minute
µm	Micrometer
Mm	Milimeter
Cm	Centimeter
W	Waat
G	Gram
Mg	Miligram
M	Meter
S	Second
mL	Mililiter
L	Liter
Ppm	Part per million
v/v	volume to volume ratio

LIST OF ABBREVIATIONS

Fe	Ferum
Ni	Nickel
Cu	Copper
TMIs	Transition Metal Ions
PLA	Polylactic Acid
PNC	Polymer Nanocomposite
MMT	Montmorrilonite
TGA	Thermal Gravimetry Analyzer
FTIR	Fourier Transform Infrared
SEM	Scanning Electron Microscopy
AAS	Atomic Absorption Spectrometry
MW	Molecular weight

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

1.1.1 Background of Polylactic Acid (PLA)

Polylactic acid or polylactide ,PLA is a type of biodegradable thermoplastic that is produced from renewable resources. It is primarily generated from dextrose, a natural sugar derived from the starch in kernels of corn. Other agricultural raw materials, such as rice, sugar beets, sugar cane, wheat and sweet potatoes, can also serve as sources for the starch or sugars used to make this biopolymer. (Averous, 2008) This means that the production of PLA can be tailored to use dominant, locally available crops. For instance, the usage of sugar canes to produce PLA in Malaysia.

Conventionally, most of the plastic products used daily are petroleum-based. Recently though, the usage of this biopolymer is garnering more favor as it boasts the ability to have clear and strong properties similar to that of oil-based plastics but with an added advantage of being commercially compostable. PLA also requires 65 percent less energy to produce and generates 68 percent fewer greenhouse gasses in comparison with traditional oil-based plastics. (Kingsland, 2010)

It is used in many fields including that of biomedicine, pharmaceutical and food packaging. Because it is biodegradable, it is primarily used in the development of bioplastic products such as loose-fill packaging, compost bags, and disposable tableware. In the food packaging industry, PLA is used to produce biodegradable and compostable disposable cups that can hold cold beverages and as the lining in cups for hot beverages. Oligolactic Acid (OLA), a shorter polymer of lactic acid is also being used as a surfactant on the pharmaceutical industry (Averous, 2008)

1.1.2 Background of Nanoclay

Nanoclays are organoclay nanoparticles of layered mineral silicates. It is divided into several types such as montmorillonite , bentonite, koalinite, and hectorite. When used in polymer nanocomposites, they have a large range of attractive applications such as rheological modifiers and gas absorbents. Montmorillonite nanoclay is the most common form of nanoclay and is in pure form. (Alexandre, 2000)

Closite Na^+ is a type of montmorillonite that consists of 1 nm thick aluminosilicate layers surface-substituted with metal cations, Na^+ and stacked in 10 µm-sized multilayered stacks. The dispersion of montmorillonite in a polymer matrix to form polymer-clay nanocomposite depends on how the surface of the clay layers are modified,. Within the nanocomposite individual clay layers fully separate to form plate-like nanoparticles with very high aspect ratio. (Olad, 2011)

Cloisite C20 is an organically modified nanoclay which has layered magnesium aluminum silicate platelets. The platelets are surface modified with dialkyldimethylammonium chloride also known as hydrogenated tallow. The alkyl from this structure is derived from hydrogenated tallow to allow complete dispersion into and provide miscibility with the thermoplastic systems for which they were designed to improve. (Southern Clay Product Bulletin, 2011)

1.1.3 Background of Clay/Polymer nanocomposites

Polymer nanocomposites(PNC) are a new class of materials which has promising potential future applications such as high-performance materials. The main feature of the polymer nanocomposite basically consists of a host polymer that is reinforced with approximately 5%wt nanosized inorganic fillers. The nanofiller will significantly impact the overall macroscopic properties of the host polymer.

There are three major classes of polymer nanocomposites that can be obtained by the use of different nanofillers; which are Clay/Polymer Nanocomposites, Metal/Polymer Nanocomposites, and Carbon Nanotubes/Polymer Nanocomposites

In the clay/polymer nanocomposite, typically smectite-type clays are used as fillers. Montmorillonite layered structures and other forms of nanoclay are dispersed in a host polymer matrix. Based on the type of bonding between the polymer chain and the silicate layer, new material showing improvement in different macroscopic aspects are achieved. (Gacitua, et. al., 2005) These macroscopic properties may include higher tensile strength and better heat and chemical resistance.

1.1.4 Background of surface modification

The main goal of this experiment is to modify the surface of nanoclay and to disperse it as a filler within PLA to form a nanocomposite. Surface modification refers to the modification reaction that occurs at the surface of a material that brings about physical, chemical or biological characteristics different from the ones originally found on the surface of a material.

The modification can be done by several different methods including:

Table 1.1: Methods of Surface Modification

Physical	Chemical	Radiation
• Physical adsorption • Langmuir-Blodgett film	• Oxidation by strong acids • Ozone treatment • Chemisorption • Flame treatment	• Plasma (glow discharge) • Corona discharge • Photo-activation (UV) • Laser • Ion/Electron beam • γ-irradiation

(Source: Loh, et al.,1995)

Nanoclay is naturally hydrophillic and is held together strong by electrostatic forces. This makes it poorly suited to mix and interact with polymer matrices. Therefore, the clay needs to be treated before it can be used to make a polymer nanocomposite. The most common way of treating clay in order to make it more compatible with polymer matrices, is through ion exchange.

1.2 PROBLEM STATEMENT

PLA is being increasingly used in industries as one of the most efficient thermoplastics. Even so, PLA is still subject to common problems such as fatigue and low maximum continuous working temperature (approximately 50º C). This narrows down its applications especially in heavy duty industries.

But most importantly, the usage/creation of this polymer nanocomposite will generate waste which could lead to pollution. If the product is biodegradable it will spend a shorter duration of time as waste, thus eliminating potential pollution.

1.3 OBJECTIVE

The objectives of this study are:-

I. To modify the surface of nanoclay filler by using transition metal ions.
II. To study the structure and characteristicss of the modified nanoclay.
III. To study the properties of PLA polymer by using the modified nanoclay as a filler.
IV. To draw a comparison between the properties of modified-nanoclay filled PLA polymer with unmodified-nanoclay filled PLA

1.4 SCOPE OF STUDY

In order to meet with the objectives of this project, the scope of study is narrowed down to the following:

I. To modify the surface of nanoclay, Cloisite Na^+ and Cloisite C20 with copper, nickel and ferum salts using the solution intercalation method.

II. To determine the best solvent-metal ion pairing to be used for the modification as well as to prove ethanol is a viable alternative for currently used solvents, dioxane and methanol.

III. To determine the structure of modified nanoclay and compare it with the structure of unmodified nanoclay.

IV. To determine the thermal stability and biodegradibility of modified nanoclay-filled PLA polymer and compare it with the properties of unmodified nanoclay-filled PLA polymer.

1.5 RATIONALE AND SIGNIFICANCE

This experiment is done in order to enhance the desirable properties of conventional PLA nanocomposites in terms of biodegradability. It is also done to prove that ethanol is a viable, less toxic alternative solvent that can be used to perform the surface modification. Quickening the biodegradability of bioplastics is also better for the environment as a material that requires a shorter period to biodegrade means will spend a shorter period time being waste products. Essentially, it will serve as more environmentally-friendly option in comparison to conventional oil-based plastics. of nanoclay.

In terms of applications, a higher thermal stability will significantly widen the usage of PLA nanocomposites in industries especially heavy duty industries which require equipments to withstand extremely high temperatures. This study will primarily be focusing on finding an alternative for conventional nanoclay polymer composites which is more biodegradeable, and yet is comparable in terms of thermal stability.

1.6 CONCLUSION

This experiment is done is hopes of discovering a more adept and commercially suited polymer nanocomposite using surface modification techniques to modify the structure of the polymer filler, nanoclay. The organoclay in this research will be modified using transition metal ions.

CHAPTER 2

LITERATURE REVIEW

2.0 INTRODUCTION

The primary goal of the current research is to modify the surface of the nanoclay filler and test the properties of the PLA nanocomposite using the modified nanoclay as a reinforcement agent. The current research will primarily be focusing on using transition metal ions (i.e Copper $^{2+}$ ions from Copper salts) to modify the surface of nanoclay, Cloisite Na^{+} and Cloisite C20A. Based on the focal point of this research, the primary raw material used can be identified as nanoclay, PLA, and transition metal ions.

2.1 POLYLACTIC ACID (PLA)

Polylactic acid (PLA) is a thermoplastic polymer that when in a solid state can be either semicrystalline or totally amorphous. Lactic acid (2-hydroxy propionic acid) is the most common form of the acid. PLA is an unique polymer that in some ways behaves similar to PET, but also to a certain extent performs a lot like polypropylene (PP). Ultimately, it can be considered as the polymer with the broadest range of applications because of its ability to be crystallized, modified, filled, copolymerized, and processed in most polymer processing equipment. It can beformed into transparent films, fibers, or injection molded into preforms like bottles. (Henton, et al., 2005). But in spite of these characteristics its commercial viability has been limited by high production costs which is approximately greater than $2/lb.

The PLA synthesis process begins with lactic acid which is produced by the fermentation of dextrose. This is followed by a continuous condensation reaction which will lead to the production of low molecular weight PLA prepolymer. Next, the low molecular weight prepolymer is then converted to high molecular weight polymers by using ring-opening polymerization. The process is depicted in the following Figure 2.1.

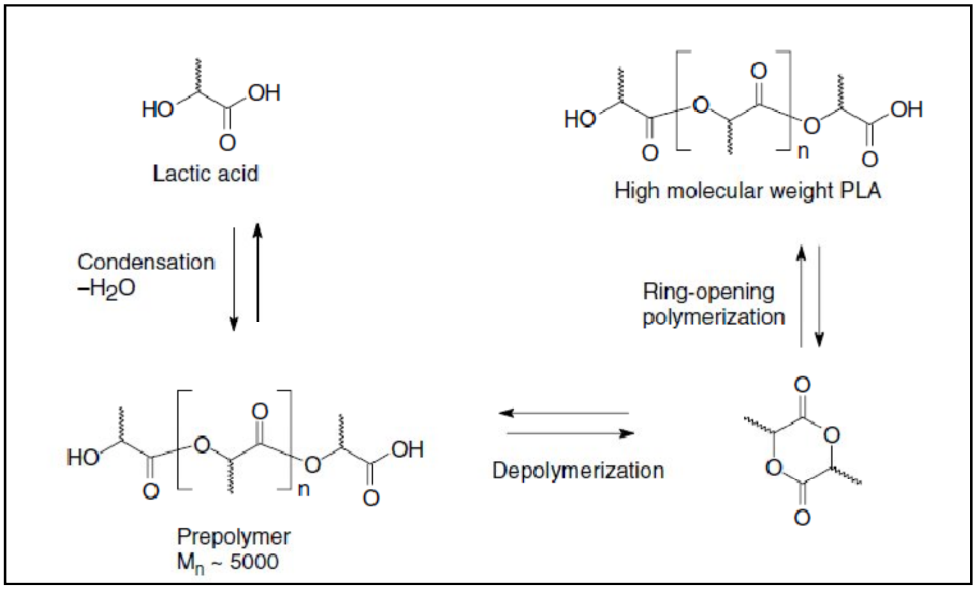

Figure 2.1: Synthesis of Polylactic Acid

(Source: Averous, 2008)

There are several reviews that detail the properties and characteristics of PLA. The physical characteristics of PLA are greatly dependent on its transition temperatures for common qualities such as density, heat capacity, and mechanical properties. When in the solid state PLA can either be amorphous or semicrystalline, depending on its stereochemistry. For amorphous PLAs, the glass transition (*T*g) determines the maximum usable temperature for commercial applications. When in the semicrystalline state, both the *T*g , which is approximately 58 °C and the melting point ,*T*m, which ranges from 130°–230°C are important when determining the usable temperature for various applications. Above the *T*g , amorphous PLAs will behave as a viscous fluid upon further heating. While below the *T*g, PLA will behave as a glass until cooled to its β transition temperature of approximately -45°C. (Henton, et. al, 005). The properties of PLA compared to other polymers are listed in Table 2.1.

Table 2.1: Properties Comparison Chart of PLA and Other Polymers.

Properties of Synthetic and Natural Fibers

Fiber Property	Nylon 6	PET	Acrylics	PLA	Rayon	Cotton	Silk	Wool
Specific gravity	1.14	1.39	1.18	1.25	1.52	1.52	1.34	1.31
Tenacity (g/d)	5.5	6.0	4.0	6.0	2.5	4.0	4.0	1.6
Moisture regain (%)	4.1	0.2–0.4	1.0–2.0	0.4–0.6	11	7.5	10	14–18
Elastic recovery (5% strain)	89	65	50	93	32	52	52	69
Flammability	Medium	High smoke	Medium	Low smoke	Burns	Burns	Burns	Burns slowly
UV resistance	Poor	Fair	Good	Good	Poor	Fair	Fair	Fair

(Source: Henton, et al., 2005)

PLA has a wide range of applications, such as woven shirts, microwavable trays, hot-fill applications and even engineering plastics. Since these blends have good structure (form)-stability and visual transparency it becomes useful as low-end packaging material. PLA is also used in biomedical applications such as in sutures, stents, drug delivery devices and as a material for tissue engineering. Because it is biodegradable, it can also be employed in the preparation of bioplastics which can be used to manufacture loose-fill packaging, compost bags, food packaging, and disposable tableware. PLA is also extremely useful when spun into fibers. These fibers are the starting material for various products such as upholstery, disposable garments, awnings, and diapers. . (Averous, 2008)

2.2 NANO-SIZED ORGANOCLAY (NANOCLAY)

One of the primary nanofillers used in polymer nanocomposites (PNC) are nanoclays. Cloisite Na^+ *(*Na^+MMT*)* and Closite C20A are types of nanoclay. Cloisite Na^+, is a type of natural,pure unmodified montmorillonite which consists of aluminosilicate layers which have been surface-substituted with metal cation, Na^+. It is made up of smectite clay minerals and has a plate-like structure. Even though the individual platelet thicknesses are generally only around one nanometer (one-billionth of a meter), nanoclay still has an extremely high aspect ratio. **(**Olad, 2011). This results in a montmorillonite that is hydrophilic in nature.

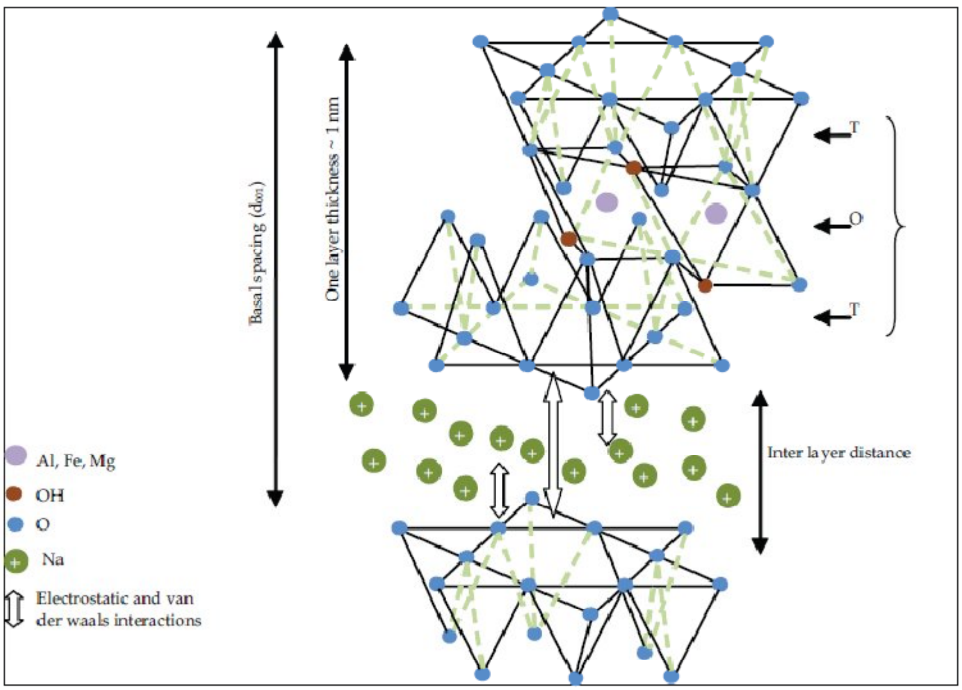

Figure 2.2: Layered Silicate Structure of Montmorillonite

(Source: Olad, 2011)

Nanotubes or Carbon nanotubes are a group of carbon molecules tubular in shape provided which have very paricular properties. The nanotubes are structured cylindrically with each of its ends covered by half a fullerene molecule. Its diameter is only a few nanometers, but its length may reach several millimeters. Several types of nanotubes exist; but they can be divided in two main categories which are single-walled (SWNT) and multi-walled (MWNT). In terms of their electrical properties, nanotubes can be either excellent conductors or insulators depending on their structure. Thermal conductivity performance is also excellent in the axial direction but remains very low in the lateral direction.. (Khare, & Bose, 2005)

Though both nanotubes and nonoclay are potentially useful fillers for polymers, this research will be focusing on the use of nanoclay (Closite Na^{+}) instead of carbon nanotubes. This is due to the cost efficiency and cost competitiveness of nanoclay in comparison with nanotubes. The significantly lower cost of nanoclay will make it a more appropriate option for large scale industrial usage.

2.3 CLAY/POLYMER NANOCOMPOSITE

Nanocomposites are prepared by dispersing a less than 5wt% nanoclay into a polymer which offers tremendous improvement in performance of the polymer. Usually smectite-type clays such as (MMT) and hectorite are used as fillers. The process of dispersing clay into a polymer structure is called exfoliation .Exfoliation is aided by the use of surface compatibilization or suface modification chemistry, which basically increases the distance between the stacks of plate-like structure in nanoclay to the extent that it may be separated easily by mechanical shear or heating.(Gacitua, et al., 2005). Nanocomposites also show excellent mechanical properties when compared to the pure polymer in terms of tensile strength, heat and chemical resistance.

Generally, a well-developed polymer/clay nanocomposite results in increased mechanical strength compared to the pure polymer matrix since uniform dispersion of the nano-sized clay particles produces a high interfacial area and ionic bonds between the nanoclay and host polymer. Currently there are several polymer nanocomposites in the market that uses clay as a filler. The applications as well as the improvement in properties brought forth by the introduction of clay into the nanocomposite are listed in Table 2.2:-

Table 2.2: List of Commercially Available Clay/Polymer Nanocomposite

APPLICATION	IMPROVEMENT OF PROPERTIES
Nylon 6 Films and Bottles	• Oxygen and CO_2 barrier • Water vapor barrier • UV transmission • Thermal stability • Stiffness • Down-gauging • Clarity • Anti-tack
Polyolefin Injection Mold	• Thermal stability • Shrinkage / warpage reduction • Stiffness • Solvent / chemical resistance • Flame resistance • Weight reduction • Fiberglass reduction • Thin-walling • Scratch and mar • Anti-bloom
Epoxy	• Higher Tg • Stiffness • Solvent / chemical resistance • Flame resistance • Rheology control • Scratch and mar • Anti-bloom